Synthesis and characterization of polyurethane coatings derived from polyols synthesized with glycerol, phthalic anhydride and oleic acid

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1. Introduction

About 90% of the polyols currently used for the production of polyurethanes (PUR) worldwide are based on polyethers derived from ethylene and propylene oxides. However, as the oil crisis and global warming deepen, there are great interests in utilizing renewable resources as substitutes for petrochemical derivatives [1,2].

Raw materials from vegetable oils are important sources for green polyols. As a matter of fact, vegetable oils have a number of excellent properties which could be utilized in producing valuable polymeric materials such as epoxy, polyesteramide, alkyd and polyurethane in addition to their many applications in other areas. Literature studies reveal many examples of synthesis of different kinds of polymeric resins made from seeds and oils of plants. Dutta et al. [3] used Nahar (a plant that produces high oil content seeds) seed oil to synthesis polyester resin. Other traditional seeds such as linseed [4], soybean [5–7], amaranth [8], castor [9–11], sunflower kernels [12], cashew nut [13] and karanja [14] have been used or still under development for the synthesis of different kinds polymeric resin.

Polyurethane materials created from vegetable oils such as cast resins and rigid foams have been in use for some time [8,15–19]. Technologies to produce polyols from palm oil and palm kernel oil that are economically competitive to petroleum-based polyols have been developed in Malaysia [20–27]. The polyols can be produced by reacting palm oil and palm kernel oil with polyhydric alcohols and carboxylic acids to obtain longer chain polyols. These polyols are then reacted with polyisocyanate to produce polyurethane. To date, polyols from palm oil have been used to produce flexible and rigid PUR foam successfully [25]. However, the effort to prepare PUR coatings from oleic acid polyols is still under development.

The present work describes the development of PUR coatings by reacting three different polyester polyols containing different percentage of oleic acid with aromatic polyisocyanate, TDI, by varying the NCO/OH ratio. The reaction of polyol and TDI was then characterized by FTIR spectroscopy. PUR coatings were applied on mild steel panels and cured under room temperature. The drying time, pencil hardness, adhesion properties, chemical/corrosion resistant behaviors and solvent rub test were measured using standard methods.

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OH as no water was evolved. At a temperature was then increased to 180–200 °C when the reaction could proceed readily with the evolution of water, which was collected at 90, respectively. The molecular weight distribution of the polyols was determined by gel permeation chromatography (GPC, Waters, polystyrene standards) in THF (elution rate: 1 ml/min) at 35 °C. The viscosity of the polyols was measured using a Brookfield model RVT plate and cone viscometer (serial no. 206505) at room temperature.

2.3. Polyurethane prepolymer synthesis

The polyol was dried under reduced pressure at 80 °C for 2 h before being poured into a three-neck flat bottom flask equipped with thermometer, dropping funnel and magnetic stirrer. Polyol was mixed with calculated amounts of toluene, surfactant (L6900) and defoamer (BYK-088). PUR prepolymer was prepared by adding the required amount of TDI dropwise into the polyol mixture at 80 °C over 3 h with constant stirring. The sample formed a viscous solution, which was then coated on a mild steel panel for further investigation at ambient temperature. The composition and designation codes of the polyurethane systems are shown in Table 2.

2.4. Preparation and testing of coatings

Coatings of PUR cured at ambient temperature, were prepared by draw down method stated in ASTM D4147-93 on mild steel panel 70 mm × 200 mm. Corrosion resistance test [28], solvent resistance test (ASTM D5402-93), adhesion test (ASTM D3359-93), water resistance test (D1647-89) and pencil hardness test (ASTM D3363-92) were conducted on the coated panels. Coating thickness was measured by Sheen – Ecostest Plus BN2, type 121-17-00. The thickness of these coatings was found to be (30 ± 5) μm. Dry-to-touch (DTT) and dry-to-hard (DTH) times were recorded at ambient temperature (28–30 °C). Corrosion tests were performed in acid (0.1 M HCl), alkali (0.1 M NaOH) and salt (5% NaCl). The coated panels were dipped in the aforementioned media at 80 °C for 1 h and then dried at room temperature for 24 h. Examination was conducted for visual evidence of softening, shrinking, detachment of film or discoloration [29].

3. Results and discussion

3.1. Characteristic of oleic acid polyols and polyurethanes

3.1.1. Oleic acid polyols

In the preparation of polyols, the reaction of phthalic anhydride involved two distinct steps. The first step was the reaction between anhydride and glycerol to form a half ester and a free carboxylic group. This ring opening of phthalic anhydride did not evolve any water and could occur quite readily at moderate temperature around 120–130 °C. There was a great excess of glycerol between anhydride and glycerol to form a half ester and a free carboxylic group. This ring opening of phthalic anhydride did not evolve any water and could occur quite readily at moderate temperature around 120–130 °C. There was a great excess of glycerol over the phthalic anhydride at the initial stage which led to the formation of a mixture of oligomers with terminal carboxylic and excess hydroxyl groups. At this stage there was no significant reaction between free --COOH and --OH as no water was evolved. At the second stage, the temperature was raised to 180–200 °C. Both

### Table 1
Composition of PA, glycerol and oleic acid used in the preparation of polyols and properties of oleic acid polyols.

<table>
<thead>
<tr>
<th>Compositions/properties</th>
<th>Alk28</th>
<th>Alk40</th>
<th>Alk65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol (g)</td>
<td>456</td>
<td>256</td>
<td>145</td>
</tr>
<tr>
<td>Phthlalic Anhydride (g)</td>
<td>700</td>
<td>338</td>
<td>103</td>
</tr>
<tr>
<td>Oleic Acid (g)</td>
<td>452</td>
<td>400</td>
<td>460</td>
</tr>
<tr>
<td>Color</td>
<td>Dark brownish</td>
<td>Brownish</td>
<td>Light brownish</td>
</tr>
<tr>
<td>Acid value (mg KOH) (g⁻¹)</td>
<td>48.2</td>
<td>40.4</td>
<td>33.5</td>
</tr>
<tr>
<td>M_w</td>
<td>2322</td>
<td>2251</td>
<td>1441</td>
</tr>
<tr>
<td>M_P</td>
<td>1171</td>
<td>1070</td>
<td>1092</td>
</tr>
<tr>
<td>Poly dispersity</td>
<td>2.44</td>
<td>2.25</td>
<td>1.68</td>
</tr>
</tbody>
</table>

M_w was determined by GPC where the column was calibrated by a series of monodisperse polystyrene standards.

### Table 2
Compositions of polyols and TDI used in the preparation of polyurethanes.

<table>
<thead>
<tr>
<th>Type of polyol</th>
<th>Designation of PU composition code</th>
<th>NCO/OH ratio</th>
<th>Amount of polyol (g)</th>
<th>Toluene (g)</th>
<th>L6900 (g)</th>
<th>BYK-088 (g)</th>
<th>Amount of isocyanates adduct (g)</th>
<th>Available NCO in prepolymer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alk28</td>
<td>PUalk28(1.2)</td>
<td>1.2</td>
<td>397.89</td>
<td>200.91</td>
<td>0.24</td>
<td>0.24</td>
<td>104.40</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>PUalk28(1.4)</td>
<td>1.4</td>
<td>397.89</td>
<td>218.27</td>
<td>0.25</td>
<td>0.25</td>
<td>121.8</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>PUalk28(1.6)</td>
<td>1.6</td>
<td>397.89</td>
<td>225.28</td>
<td>0.26</td>
<td>0.26</td>
<td>139.20</td>
<td>28.5</td>
</tr>
<tr>
<td>Alk40</td>
<td>PUalk40(1.2)</td>
<td>1.2</td>
<td>399.59</td>
<td>211.68</td>
<td>0.24</td>
<td>0.24</td>
<td>104.40</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>PUalk40(1.4)</td>
<td>1.4</td>
<td>399.59</td>
<td>218.98</td>
<td>0.25</td>
<td>0.25</td>
<td>121.8</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>PUalk40(1.6)</td>
<td>1.6</td>
<td>399.59</td>
<td>221.58</td>
<td>0.26</td>
<td>0.26</td>
<td>139.20</td>
<td>28.5</td>
</tr>
<tr>
<td>Alk65</td>
<td>PUalk65(1.2)</td>
<td>1.2</td>
<td>400.46</td>
<td>262.53</td>
<td>0.24</td>
<td>0.24</td>
<td>104.40</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>PUalk65(1.4)</td>
<td>1.4</td>
<td>400.46</td>
<td>271.58</td>
<td>0.25</td>
<td>0.25</td>
<td>121.8</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>PUalk65(1.6)</td>
<td>1.6</td>
<td>400.46</td>
<td>280.62</td>
<td>0.26</td>
<td>0.26</td>
<td>139.20</td>
<td>28.4</td>
</tr>
</tbody>
</table>
the carboxylic acid of the half ester and oleic acid would compete to react with hydroxyl group to form ester with liberation of water. The oleic acid was incorporated as flexible side chains. The resulting low molecular weight polyols were viscous liquids. From the results, it can be noted that viscosity and molecular weight of the resin decreases as the oleic acid content increases. These steps and the predicted polyols structure are represented in Scheme 1 which has been published in Ref. [30].

A comparison of these polyols with a few other vegetable polyols published in Ref. [31] was summarized in Table 3.

The general properties of these polyols were quite similar to each other.

3.1.2. Polyurethanes

The coating was cured by chemical reactions of –NCO group with –OH group as represented in Scheme 2.

The extremely thin coat (30 μm) on the steel panel allows the toluene to evaporate off fairly quickly.

In this system, prepolymer were prepared with unreacted terminated isocyanate groups that could react with atmospheric moisture to form the finished crosslinked urea groups. Formation of film which was non-sticky to touch, after 48 h curing required the use of excess equivalent amount of isocyanate. Presumably the excess of disiocyanate (for NCO/OH ratio of 1.2–1.6) could introduce urea structures, which were effectively crosslinked the polymer chains.

3.2. Infrared spectroscopy

The FTIR spectra of oleic acid, Alk28, Alk40 and Alk65 were as shown in Fig. 1. The OH stretching band at 3460–3480 cm\(^{-1}\) indicates the presence of free hydroxyl groups which is observable in all the polyols except for oleic acid. Their relative intensities were quite similar as they were with similar hydroxyl value. Furthermore, typical ester C=O peak was observed at 1730 cm\(^{-1}\) and twin peak at 1580 and 1599 cm\(^{-1}\) shows conjugation of C=O with the phenyl ring from PA.

Table 3 showed the FTIR spectra of PUalk28, PUalk40 and PUalk65. A small broad peak in the range of 3500–3150 cm\(^{-1}\) appeared from the formation of NH of the urethane linkage while the –OH band at 3470 cm\(^{-1}\) of the corresponding polyols has disappeared. This was consistent with the reaction of –OH with –NCO.

<table>
<thead>
<tr>
<th>Polyols based on vegetable oil</th>
<th>Hydroxyl value (mg KOH/g)</th>
<th>(M_n)</th>
<th>Functionality</th>
<th>Viscosity at room temperature (cps)</th>
<th>(T_m) (°C) (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola [31]</td>
<td>174</td>
<td>1123</td>
<td>3.30</td>
<td>2940</td>
<td>–36</td>
</tr>
<tr>
<td>Midoleic sunflower [31]</td>
<td>164</td>
<td>1191</td>
<td>3.08</td>
<td>1850</td>
<td>–38</td>
</tr>
<tr>
<td>Soybean [31]</td>
<td>179</td>
<td>1249</td>
<td>3.47</td>
<td>3350</td>
<td>–32</td>
</tr>
<tr>
<td>Linseed [31]</td>
<td>248</td>
<td>1274</td>
<td>5.21</td>
<td>1820</td>
<td>–24</td>
</tr>
<tr>
<td>Sunflower [31]</td>
<td>178</td>
<td>1302</td>
<td>3.47</td>
<td>4080</td>
<td>–34</td>
</tr>
<tr>
<td>Corn [31]</td>
<td>179</td>
<td>1180</td>
<td>3.44</td>
<td>2710</td>
<td>–35</td>
</tr>
<tr>
<td>Alk28</td>
<td>132</td>
<td>953</td>
<td>2.24</td>
<td>12800</td>
<td>–28</td>
</tr>
<tr>
<td>Alk40</td>
<td>134</td>
<td>999</td>
<td>2.39</td>
<td>8000</td>
<td>–29</td>
</tr>
<tr>
<td>Alk65</td>
<td>135</td>
<td>859</td>
<td>2.07</td>
<td>2800</td>
<td>–28</td>
</tr>
</tbody>
</table>
3.3. Physico-mechanical and corrosion resistant characteristic of palm oil-based polyurethane coatings

Dry-to-touch and dry-hard times for the specified samples were summarized in Table 4. Coatings based on formulation of Alk28 achieved the shortest curing time, followed by Alk40 and Alk65. Pualk28 with polyol of the lowest oleic acid content cured in few seconds compared to Pualk65 with polyol of the highest oleic acid content that required few days to cure. Dry-to-touch and dry-hard times of coatings were very much dependent upon NCO/OH ratios and the oleic acid content of the polyol. More oleic acid side chains in the structure introduce greater amount of steric hindrance for the isocyanate to react with OH, hence slowing down the rate of reaction. The increment of NCO/OH ratio is relative to amount of isocyanate which consequently increases the reaction rate. As we increase the two parameters concurrently, there is a competing effect between the two parameters which results in contrasting reaction rate.

The results of pencil hardness test on the clear PUR coatings are summarized in Table 4. Generally, the pencil hardness increased as the oleic acid content of the polyols decreased. For specific composition such as Pualk28 and Pualk40, the pencil hardness increased with the NCO/OH ratios. In the case for Pualk65, the NCO/OH ratio did not affect the hardness of the coating. Hence, from the results it can be concluded that Pualk2816 had the best hardness followed by Pualk4016 and lastly Pualk6516.

Adhesion test assess the adherent strength of the cured film. A criss-cross lattice pattern with five cuts in each direction was made. An adhesive tape was placed over the grid and removed within 90 s in an angle as close as 180° as possible. The grid area was inspected for removal of coating from the substrate. Excellent adhesion performance is denoted by 0% detachment while poor performance

Scheme 2. Reaction of polyols with isocyanates to form polyurethanes [30].

Fig. 1. IR spectra showing the successful synthesis of alkyl polyols from oleic acid.

Fig. 2. IR spectra of oleic acid-based polyurethane with NCO/OH ratio of 1.6.
denoted by 65% detachment. Overall all the PUR samples exhibit excellent adhesion performance on mild steel panel.

Pualk28 performed satisfactorily under solvent rub test and was unaffected under 25 rubs of solvents such as acetone, methyl ethyl ketone and ethyl acetate. However for Pualk40, there was a slight deterioration and Pualk65 showed the worst deterioration in the solvent rub test, where loss of glossiness and detachment of films were observed. The lower molecular weight and functionality and higher amount of flexible side chain of the sample has rendered the film less compact and resulting in a less dense crosslinked network.

PUR films from Alk28 have better water resistance compared to the rest. Films of Pualk40 and Pualk65 could be detached from the mild steel panel immersed in the water for 18 h at room temperature. The water resistance improved with higher NCO/OH ratios. Alkali had greater detrimental effect on the coating than acid. PUR based on highly crosslinked polyester polyol had better chemical resistance than PUR with less crosslinked structure. As the NCO/OH ratio increased the sample became more resistance to alkali solution due to higher extend of crosslinking reaction which form a more stable physical network [32].

Salt resistance of PUR coating was poor compared to acid and alkali resistance. Wrinkled spots were observed on the films after immersion of panels in the salt solution for 1 h.

4. Conclusion

The PUR prepolymers synthesized from oleic acid polyols and toluene diisocyanate could be cured at ambient temperature by the variation of oleic acid content in polyols and NCO/OH ratio of the coatings was increased. Overall, the good film properties reflect the physico-mechanical and anticorrosive properties of all the coatings had improved. Overall, the good film properties reflect the possiblity of the oleic acid polyols-based PURs in surface coating applications. Understanding the changes in film properties due to the variation of oleic acid content in polyols and NCO/OH ratio of PUR could be useful for designing the formulation of the desired performance.

References